POTENTIAL EXPOSURE OF WORKERS TO SELECTED PESTICIDES AND DEFOLIANTS WHILE HARVESTING COTTON - IMPERIAL VALLEY, 1983

By

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SUMMARY

Monitoring of the potential inhalation exposure of cotton harvest workers to selected pesticides and defoliants was conducted during the harvest of ten fields in Imperial County in 1983-84. This monitoring was conducted as part of a study to determine harvest worker exposure to chlordimeform residues at harvest which was described in a separate report. Residue levels for twelve chemicals were measured by collecting cotton boll samples from each field just prior to the application of defoliants and at harvest. Potential inhalation exposure to the residue was measured by breathing zone air sampling for 17 man-days of harvest, 3 man-days of second harvest and 6 man-days of scrapping. At harvest, only three pesticides were present in boll samples above CDFA's laboratory's limit of detection and no organophosphate or pyrethroid was present in any breathing zone sample above the limit of detection. Defoliant residues were present in varying amounts in all day of harvest boll samples, but were not present above the limit of detection (DEF) or not appreciably above background levels (arsenic) for any breathing zone sample. This study shows that for the 12 chemicals measured, residues at harvest did not pose an inhalation hazard to cotton harvest workers.

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*Other members of the Worker Health & Safety Unit that worked on this project include: Steve Kilgore, Don Richmond, Deborah Welp, Harvard Fong, Frank Schneider, and Dorothy Alcoser.

INTRODUCTION

Heavy insect pressure in California's cotton growing areas over recent years has forced growers to use increasing amounts and types of broad-spectrum pesticides. Because of their broad-spectrum nature, large numbers of beneficial insects are killed, in addition to the target pests, when these pesticides are applied. In early 1982, Imperial County began an integrated pest management (IPM) program, in an attempt to reduce the amount of pesticides needed to control the major cotton pests - pink bollworm (Pectinophora gossypiella), cotton bollworm (Heliothis zea), and tobacco budworm (H. virescens). As a part of the IPM program, the California Department of Food 7and Agriculture (CDFA) allowed the use of chlordimeform as a Special Local Need (SLN) registration for a maximum of five growing seasons in Imperial County in 1982; Riverside County was included in the SLN in 1983. Chlordimeform is registered as effective against Heliothis. It may also help control resistant mites and their eggs, many lepidopterous insect pests, pink bollworm, and whiteflies.

Because chlordimeform is considered to be a potential human carcinogen, its use in Imperial County during the 1982 cotton season was closely monitored by the Worker Health and Safety Unit (WH&S). The workers applying the material were studied during a trial application (1), during the actual application (2), and during specific operations, such as flagging and scouting (3). In addition, cotton bolls were sampled throughout the season to determine the rate of degradation of chlordimeform in order to establish or adjust the worker reentry interval (4). The 1982 monitoring of harvest worker exposure was done during the harvest of the same fields that were followed by weekly boll sampling (5). This monitoring consisted of operator breathing zone (OBZ) air samples to measure the workers' potential inhalation exposures, and air samples taken outside the harvester cab to compare values obtained in these locations with those inside the cab. Fifteen man-days of monitoring were conducted, and no airborne levels of chlordimeform were seen down to the minimum detection level (MDL). Urine samples were obtained for fourteen man-days to measure actual exposure, with no chlordimeform metabolite detected in any of the samples. The final cotton boll samples, obtained from the treated fields at harvest, showed that the chlordimeform levels had degraded to below the MDL. However, because the harvest of the 1982 cotton was delayed approximately two months due to unseasonable rains, results of this study could not be considered typical.

A second harvest study was conducted the following cotton season (1983), with harvest occurring primarily during November and December. In addition to chlordimeform (6), measurements of aflatoxins levels present in the fields and in harvest workers' breathing zones were obtained as part of a risk assessment, to determine if the use of a suspect carcinogen (chlordimeform) can have some impact on reducing worker exposure to more potent carcinogens (aflatoxins). These measurements will be correlated to relative insect damage of each field to determine if a relationship exists between the degree of insect damage and aflatoxins levels (7).

A wide variety of pesticides are used in conjunction with chlordimeform for cotton pest control, along with several types of defoliants. In 1978, the National Institute for Occupational Safety and Health (NIOSH) conducted sampling to assess harvest worker exposure to DEF, a commonly used cotton defoliant (8). However, no information is available to characterize what

residue levels of the other chemicals are present at harvest. Sampling was done at the same time chlordimeform was monitored to determine what residue levels are present at harvest, and if these levels are significant enough to pose a health hazard.

MATERIALS AND METHODS

Monitoring was conducted during the harvest of six chlordimeform treated and four designated control fields. The treated fields had received from six to ten chlordimeform applications, with the last application approximately two months prior to harvest. Monitored fields were selected from 49 fields chosen at random by Imperial County Agricultural Commissioners' Biologists. These fields were checked weekly during the growing season by the county biologists to assess pink bollworm damage. In selecting the fields to be monitored, an attempt was made to further randomize by choosing fields in various parts of the Imperial Valley. The locations of the control fields were not as random as hoped for, as many of the original 49 fields received chlordimeform treatment before the end of the season. All of the fields were harvested using closed-cab harvesters, with mechanical module-makers used to compress the harvested cotton into large free-standing units. Prior to the onset of monitoring, County records were checked to determine what pesticides were applied to these ten cotton fields during the growing season. A total of twelve different chemicals had been used on the selected fields which could be analyzed by the CDFA Laboratory: six organophosphates, three pyrethroids, and three defoliants. To determine the residue levels of the twelve chemicals on the cotton at the time of harvest, 24 open bolls were taken on a diagonal across each field the day harvesting was monitored. These levels were compared to results from an earlier set of similiar samples taken from the same fields just after the last chlordimeform application, but prior to the application of defoliants.

Potential inhalation exposure to pesticide residues was measured using MSA Model TD and MSA Model S portable air pumps. For the first and second harvest, and scrapping operations, air was sampled in the OBZ using a 37 mm glass fiber filter, 0.3 um pore size (SKC, Inc.), at a rate of 2 L/minute. Separate samples were collected to measure the OBZ levels of cacodylic acid, an organic arsenical pesticide used as a defoliant. These samples were collected using the same type pump models, air filters, and flow rates described previously. A total of 26 OBZ samples were collected: 17 man-days of harvest, 3 man-days of second harvest, and 6 man-days of scrapping.

During the monitoring of the last field to be harvested (field #10), two cloth patches were placed on the floor inside the harvester cab, and two on a level surface outside the cab. One patch from each collection site was analyzed for pesticide residues; the other was analyzed for arsenic. This was done as a means of collecting pesticide residues adsorbed to particles larger than those collected in the air samples. The levels found on the patches placed inside the cab were compared to those found on patches outside the cab. The patches were constructed of an outer layer of seven-ounce 65 percent dacron polyester, 35 percent cotton twill, and a middle layer of 100 percent cotton gauze backed by a layer of aluminum foil. Each patch had a pre-marked area of 49 cm^2, which was cut out at the completion of the harvesting. The three layers of each patch were analyzed as one sample.

Pre- and post-work urine samples were collected from all cooperative harvester operators in 500 mL polypropylene bottles to determine chlordimeform metabolite levels. Urine was also analyzed for elemental arsenic as a means of monitoring worker exposure to cacodylic acid. The ratio of arsenic levels in the urine samples to the total volume collected was calculated for each worker. Using this ratio, and assuming the urinary excretion rate for the standard man is 1,400 mL/day (9), an estimate of daily arsenic excretion was calculated for each worker.

Air samples were kept cool and dry; patch, cotton boll, and urine samples were stored on ice until delivery to the CDFA Laboratory in Sacramento.

RESULTS

Table I shows the pesticide residues present in the breathing zone air samples during various phases of harvesting: harvest, second harvest, and scrapping. Residue levels for cotton bolls sampled at pre-defoliation and on the day of harvest are included. Cloth patch results for field #10 are also included in this table.

Table II shows elemental arsenic levels found in breathing zone air samples taken during harvest, second harvest, and scrapping. Arsenic levels for bolls collected the day of harvest, and levels on cloth patches, during the harvest of field #10, are also included.

Table III is a list of pre- and post-work urinary arsenic levels of the harvest workers. These levels are expressed in ug and ppb, with the total volume of each sample given in mL. Estimates of daily urinary arsenic excretions, calculated for each worker, are also included.

Table IV lists the pesticides which were studied according to their category, and the man-days of harvest and scrapping monitored for each.

Table V lists the treatment histories for each field.

Appendices I through III list the laboratory analytical methods.

DISCUSSION AND CONCLUSIONS

With only three exceptions, pesticide residue levels on cotton bolls had degraded to below the laboratory's limits of detection by harvest. One field had chlorpyrifos boll levels of 277 ppb at pre-defoliation, with 200 ppb remaining at harvest. Cotton from a second field had less than 100 ppb chlorpyrifos present prior to defoliation; harvest samples had levels of 230 ppb. In a third field, curacron was present at a higher level in the harvest sample (6,100 ppb) than was found pre-defoliation (1,600 ppb). No explanation can be given for the increased levels of pesticide residue levels seen in the day of harvest samples from the two fields. DEF was present in varying amounts (400-2,200 ppb) on all day of harvest boll samples.

None of the OBZ samples collected during the harvest, second harvest, and scrapping operations had organophosphate, pyrethroid, or Harvade residue levels above the limits of detection. OBZ levels of cacodylic acid, ana-

lyzed as elemental arsenic, ranged from N.D. to 0.24 ug/m^3. The fields with the highest levels were those on which cacodylic acid had been used as one of the defoliants. Four of the fields not treated with cacodylic acid also had measurable amounts of arsenic in the OBZ samples. This may be a background level, due to the naturally occurring arsenic levels in the soil. Even though DEF was present on the cotton bolls at harvest, no OBZ samples contained levels above the limit of detection (1.0 ug/sample). Previous studies of airborne DEF levels at harvest ranged from 7-1,068 ng/m^3 (8).

In an attempt to see if DEF and cacodylic acid residues adsorbed to larger-sized particles than those collected during personnel air sampling, cloth patches were placed on level surfaces inside and outside the harvester cabs. Ideally, the patches inside the cabs should be protected from large particles, such as plant matter. However, in actual practice, the windows and door of the cab are often left open during harvesting. The patches from both locations were covered with dirt and plant debris by the end of the sampling period. There was no significant difference in the arsenic levels seen on the patches placed inside the cab (0.08 and 0.09 ug) as compared with those outside the cab (0.06 and 0.09 ug). Both inside patches analyzed for DEF were below the limit of detection. DEF levels from the outside patches were 0.7 and 1.4 ug. This may indicate that DEF adsorbs to particles larger than those collected during the OBZ monitoring; although, no conclusions can be drawn on such limited data.

Urine samples, collected for chlordimeform metabolite analysis before and after work, were screened for arsenic. From the levels found, an estimate was made of daily arsenic excretion for each worker. These values, ranging from 3 to 26 ug/day, are comparable to the background level of less than 20 ug/day (9).

The results of this study indicate that the pesticide residues present at harvest did not pose an inhalation hazard to cotton harvest workers. These workers were exposed to some arsenic levels, but the highest OBZ measurement (0.24 ug/m^3) is far below the present occupational standards of 10 ug/m^3 (inorganic arsenic) or 500 ug/m^3 (organic arsenic). Any further studies on cacodylic acid or other organic arsenical compound should be analyzed for the specific organic arsenic. By doing this, it would be possible to distinguish the level of exposure from naturally occurring background arsenic levels.

TABLE I

Pesticide Residues on Cotton Bolls and Air Filters

Field	Pre-Defoliation Bolls (ppb)	Day of Harvest Bolls (ppb)	Filters (ug/m^3)				
Number 1	10-31	12-6	12-6		12-20	12-20	
			Man-Day 1	Man-Day 2	2nd Harvest	Scrapping Man-Day 1	Scrapping Man-Day 2
DEF	NT	NT	ND	ND	ND	ND	ND
Number 2	10-17	12-7	12-7		12-8	12-12	
			Man-Day 1		Man-Day 2	Scrapping	
DEF	NT	NT	ND		ND	ND	
Pydrin	ND	ND	ND		ND	ND	
Lorsban	277	200	ND		ND	ND	
Bolstar	200	ND	ND		ND	ND	
Ambush	353	ND	ND		ND	ND	
Number 3	11-1	12-7	12-8		12-9		
			Man-Day 1		Man-Day 2		
Dursban	140	ND	ND		ND		
Pydrin	1,070	ND	ND		ND		
DEF	NT	760	ND		ND		
Bolstar	500	ND	ND		ND		
Guthion	ND	ND	ND		ND		
Number 4	11-3	12-13	12-13		12-13		
			Man-Day 1		Man-Day 2		
Dursban	ND	230	ND		ND		
DEF	NT	1,080	ND		ND		
Ambush	660	ND	ND		ND		
Bolstar	ND	ND	ND		ND		
Number 5	10-27	12-8	12-15 (2nd Harvest)				
			Man-Day 1		Man-Day 2		
DEF	NT	2,200	ND		ND		
Pydrin	NT	NT	ND		ND		

TABLE I (CONT'D)

Pesticide Residues on Cotton Bolls and Air Filters

Field	Pre-Defoliation Bolls (ppb)	Day of Harvest Bolls (ppb)	Day of Harvest Filters (ug/m^3)		
Number 6	10-27	12-19	12-22	12-22	
			Man-Day 1	Man-Day 2	
Dursban	ND	ND	ND	ND	
Ambush	640	ND	ND	ND	
DEF	NT	400	ND	ND	
Cymbush	ND	ND	ND	ND	
Number 7	10-13	11-18	11-21	Scrapping 11-22	
				Man-Day 1	Man-Day 2
Ambush	2,010	ND	NT	ND	ND
Pydrin	ND	ND	NT	ND	ND
Bolstar	223	ND	NT	ND	ND
Dursban	ND	ND	NT	ND	ND
DEF	NT	1,270	NT	ND	ND
Malathion*	NT	NT	NT	ND	ND
Number 8	10-20	11-30	11-30	12-6	12-14
			Man-Day 1	Man-Day 2	Scrapper
Dursban	NT	NT	NT	NT	ND
Curacron	1,600	6,100	ND	ND	NT
Me Parathion	450	ND	ND	ND	NT
Guthion	ND	ND	ND	ND	NT
DEF	NT	NT	NT	ND	ND
Number 9	10-19	12-23	12-23		
Ambush	ND	ND	ND		
Dursban	340	ND	ND		
Harvade	NT	ND	ND		

TABLE I (CONT'D)

Pesticide Residues on Cotton Bolls and Air Filters

Field	Pre-Defoliation Bolls (ppb)	Day of Harvest Bolls (ppb)	Filters (ug/m^3)		
			Man-Day 1	Man-Day 2	Patches Outside/In
Number 10	10-27	1-4	1-4	1-4	1-4
DEF	NT	1,600	ND	ND	DEF 0.7 UG/ND
Bolstar	140	ND	ND	ND	DEF 1.4 UG/ND
Pydrin	14,670	ND	ND	ND	

* Scrapping was interrupted so malathion could be applied for boll weevil control.

ND = None Detected
NT = Not Tested

MDL for filters in ug/sample:

Guthion	2.6	Pydrin	0.3
Ambush	0.2	Bolstar	0.4
Curacron	0.1	DEF	1.0
Parathion	0.1	Dursban	0.1
Cymbush	0.2	Malathion	0.5
Harvade	0.4		

MDL for cotton bolls/sample

Guthion	500 ppb (5 ug/10 g sample)
Pydrin	1000 ppb (10 ug/10 g sample)
Ambush	300 ppb (3 ug/10 g sample)
Curacron	100 ppb (1 ug/10 g sample)
Parathion	100 ppb (1 ug/10 g sample)
Cymbush	100 ppb (1 ug/10 g sample)
Harvade	500 ppb (5 ug/10 g sample)
Dursban	100 ppb (1 ug/10 g sample)
Bolstar	100 ppb (1 ug/10 g sample)

MDL for patch:

DEF 0.4 ug/sample

TABLE II

Elemental Arsenic Levels in Cotton Fields at Harvest

Field	Sampling Dates	Breathing Zone Air Levels* (ug/m^3)/Time	Sample Type	Boll Levels (ppb)
Number 1	12-6	0.05/385	harvest	NS
		0.07/385	harvest	
	12-20	ND/255	second harvest	
		ND/255	scrapping	
		ND/282	scrapping	
Number 2	12-7	0.09/206	harvest	NS
	12-8	0.05/370	harvest	
	12-12	ND/385	scrapping	
Number 3	12-8	0.03/391	harvest	NS
	12-9	0.04/370	harvest	
Number 4	12-13	ND/420	harvest	NS
		ND/450	harvest	
Number 5	12-15	ND/325	second harvest	NS
		ND/325	second harvest	
Number 6	12-22	ND/503	harvest	200
	12-22	ND/505	harvest	
Number 7 treated with cacodylic acid 10-27	11-18	0.11/450	harvest	3,900
		0.12/465	harvest	
	11-22	0.12/420	scrapping	
		0.24/420	scrapping	
Number 8	11-30	0.06/328	harvest	NS
	12-6	0.06/510	harvest	
	12-14	ND/170	scrapping	
Number 9 treated with cacodylic acid 10-27	12-23	0.15/170	harvest	7,900

TABLE II (CONT'D)

Elemental Arsenic Levels in Cotton Fields at Harvest

Field	Sampling Dates	Breathing Zone Air Levels	Sample Type	Boll Levels (ppb)
Number 10	1-4	ND/360	harvest	2,000
	1-4	0.03/360	harvest cotton patch inside harvester 0.09 ug cotton patch inside harvester 0.08 ug cotton patch outside harvester 0.09 ug cotton patch outside harvester 0.06 ug	

*Breathing Zone Air Levels calculated as (ug/m^3)/sampling period in minutes.

ND = None Detected
NS = Not Sampled

MDL Filters = 0.02 ug/sample
MDL Bolls = 20 ppb
MDL Patches = 0.02 ug/sample

TABLE III

Urinary Arsenic Levels of Harvest Workers

Field and Date	Pre-Work			Post-Work			Estimated Arsenic* Excretion Per Day
	ppb	mL	ug	ppb	mL	ug	ug
Number 1							
12-6	15	128	1.9	21	167	3.5	25.6
	13	148	1.9	8	178	1.4	14.2
Number 2							
12-7	15	220	3.3	16	163	2.6	21.5
Number 3							
12-8	No Sample			12	103	1.2	16.3
12-9	8	79	0.6	12	97	1.2	14.3
Number 4							
12-13	10	98	1.0	10	52	0.5	14.0
	10	182	1.8	4	106	0.4	10.7
Number 5							
12-15	14	191	2.7	6	66	0.4	16.9
	No Sample			13	140	1.8	18.2
Number 8							
12-6	2	223	0.4	2	171	0.3	2.5

a/ The volume for these samples was not measured.

*The ratio of arsenic levels in the urine samples to the total volume collected was calculated for each worker. Using this ratio, and assuming the urinary excretion rate for the standard man is 1,400 mL (9), an estimate of daily arsenic excretion was calculated for each worker as follows:

$$\frac{[\text{pre-work sample (ug)} + \text{post-work sample (ug)}]}{[\text{pre-work sample (mL)} + \text{post-work sample (mL)}]} \times 1{,}400 \text{ mL/day} = \text{Estimated Arsenic Excretion per day}$$

MDL = 2 ppb or 3 ug

TABLE IV

Man-Days of Monitoring Conducted for Each Pesticide

Pesticide	Harvest/Second Harvest	Scrapping
Organophosphates:		
Bolstar	8	3
Curacron	2	1
Dursban/Lorsban	9	4
Guthion	4	0
Malathion	0	2
Parathion	2	0
Pyrethroids:		
Ambush	7	3
Cymbush	2	0
Pydrin	8	3
Defoliants:		
DEF/Folex	16	6
Harvade	1	0
Cacodylic Acid	20	5

TABLE V

FIELD TREATMENT HISTORIES

Field # 1 Acres 53

Date Applied	Pesticide
5/7	Kelthane-Sulfur 3-50
5/27	No Mate
6/7	No Mate
6/13	No Mate
6/18	No Mate, Bio-tac
6/23	No Mate, Bio-tac
6/28	No Mate, Bio-tac
7/2	No Mate, Bio-tac
7/3	Supracide
7/7	No Mate, Bio-tac
7/10	No Mate, Bio-tac
7/13	Supracide
7/19	Pydrin
7/29	Pydrin, Fundal
8/7	Pydrin
8/13	Pydrin, Fundal
8/21	Pydrin, Fundal
9/8	Bolstar, Fundal
9/16	Pydrin, Fundal
10/28	DEF

Predefoliation Boll Samples Collected: 10/27/83

Day of Harvest Boll Samples Collected: 12/06/83

Harvest Worker Exposure Monitoring Conducted: 12/06/83, 12/20/83

Field	Acres

Date Applied	Pesticide
3/31	Dacthal
7/9	Temik
7/12	Lorsban
7/15	Temik
7/26	Ambush
8/5	Galecron, Ambush
8/12	Pydrin, Fundal
8/20	Ambush, Galecron
8/27	Pydrin, Fundal
9/3	Lorsban
9/8	Ambush, Galecron
9/16	Lorsban, Galecron
9/28	Bolstar
10/18	DEF
11/5	Leafex

Predefoliation Boll Samples Collected: 10/13/83

Day of Harvest Boll Samples Collected: 12/07/83

Harvest Worker Exposure Monitoring Conducted: 12/07/83, 12/08/83, 12/12/83

Field # 3 Acres 70

Date Applied	Pesticide
3/23	Treflan
6/28	Temik
6/30	Guthion
7/2	Supracide, Malathion, Caparol
7/9	Supracide
7/22	Supracide, Comite
7/28	Fundal, Pydrin
8/7	Fundal, Pydrin
8/13	Fundal, Comite
8/19	Guthion
8/25	Pydrin, Fundal
9/3	Lorsban, Fundal
9/10	Pydrin, Fundal
9/15	Pydrin, Fundal
9/27	Lorsban, Galecron
9/28	Lorsban, Galecron
?	Bolstar
11/1	DEF
11/23	Leafex

Predefoliation Boll Samples Collected: 11/01/83

Day of Harvest Boll Samples Collected: 12/07/83

Harvest Worker Exposure Monitoring Conducted: 12/08/83, 12/09/83

Field # 4 Acres 98

Date Applied	Pesticide
4/8	Prefar, Caparol, Disyston Pebbles
5/7	Azodrin
6/28	Caparol, Treflan
7/9	Supracide
7/20	Supracide, Dylox
7/27	Supracice, Chlordimeform
7/28	Fundal, Supracide
8/5	Supracide, Fundal
8/11	Bolstar, Fundal
8/19	Bolstar, Galecron
9/3	Lorsban, Galecron
9/10	Bolstar, Galecron
9/19	Bolstar, Fundal
9/27	Bolstar, Galecron
10/6	Ambush, Galecron
11/3	DEF
11/19	Leafex

Predefoliation Boll Samples Collected: 11/03/83

Day of Harvest Boll Samples Collected: 12/13/83

Harvest Worker Exposure Monitoring Conducted: 12/13/83

Field # 5 Acres 30

Date Applied	Pesticide
5/17	No Mate
6/1	No Mate
6/7	No Mate
6/13	No Mate
6/18	No Mate, Bio-tac
6/23	No Mate, Bio-tac
6/28	No Mate, Bio-tac
6/30	Supracide
7/2	No Mate, Bio-tac
7/7	No Mate, Bio-tac
7/8	Supracide, Fundal
7/15	Supracide
7/28	Pydrin, Fundal
8/11	Pydrin, Fundal
8/23	Pydrin, Fundal
9/3	Pydrin, Fundal
9/9	Pydrin, Fundal
9/17	Pydrin, Fundal
10/8	Pydrin, Fundal
10/28	DEF, Leafex

Predefoliation Boll Samples Collected: 10/27/83

Harvest Boll Samples Collected: 12/08/83

Harvest Worker Exposure Monitoring Conducted: 12/15/83

Field # 6 Acres 17

Date Applied	Pesticide
4/8	Treflan, Caparol
4/30	Dacthal
7/7	Treflan, Caparol
7/21	Supracide, Orthene
7/29	Supracide, Orthene
8/10	Supracide, Fundal
8/19	Fundal, Cymbush
8/25	Lorsban, Cymbush, Fundal
9/1	Cymbush, Lorsban, Fundal
9/8	Lorsban, Fundal, Cymbush
9/15	Cymbush, Lorsban, Fundal
9/29	Ambush, Fundal
10/3	Ambush, Fundal
10/28	DEF 6
11/14	Accelerate

Predefoliation Boll Samples Collected: 10/27/83

Harvest Boll Samples Collected: 12/19/83

Harvest Worker Exposure Monitoring Conducted: 12/22/83

Field # 7 Acres 104

Date Applied	Pesticide
2/11	Imidan 50, Dimethoate
3/27	Little Pebbles
4/30	Azodrin
5/6	Kelthane Sulfur
5/13	Kelthane Sulfur
6/21	No Mate, Bio-tac
7/2	No Mate, Bio-tac
7/10	Supracide, Orthene
7/13	No Mate, Bio-tac
7/19	Supracide
8/4	Ambush, Comite, Cotton Seed Oil
8/14	Ambush, Comite, Cotton Seed Oil
8/25	Pydrin, Cotton Seed Oil
9/1	Ambush, Cotton Seed Oil
9/10	Ambush, Cotton Seed Oil
9/19	Ambush, Cotton Seed Oil
9/29	Bolstar, Comite
10/17	DEF 6
10/27	Cotton Aid, Leafex
11/22	Malathion

Predefoliation Boll Samples Collected: 10/13/83

Harvest Boll Samples Collected: 11/18/83

Harvest Worker Exposure Monitoring Conducted: 11/18/83, 11/22/83

Field # 8 Acres 40

Date Applied	Pesticide
4/19	Dacthal, Caparol
5/3	Parathion, Lorsban
6/24	Treflan, Bladex
7/12	Lorsban
7/19	Lorsban
7/26	Lorsban
8/2	Lorsban
8/27	Thiodan, Methyl Parathion 5
9/2	Curacron, Methyl Parathion 5
9/12	Curacron, Methyl Parathion 5
9/17	Guthion, Comite
9/24	Curacron, Methyl Parathion 5
9/30	Curacron, Methyl Parathion 5
10/8	Curacron, Methyl Parathion 5
10/20	DEF
11/8	Paraquat

Predefoliation Boll Samples Collected: 10/20/83

Harvest Boll Samples Collected: 11/30/83

Harvest Worker Exposure Monitoring Conducted: 11/30/83, 12/14/83

Field # 9 Acres 20

Date	Pesticide
3/23	Treflan
6/15	Temik
7/3	Lorsban
7/13	Guthion, Malathion
7/21	Guthion, Malathion
8/4	Ambush
8/13	Ambush
8/24	Ambush
9/1	Ambush
9/11	Lorsban
11/15	Harvade, Accelerate

Predefoliation Boll Samples Collected: 10/19/83

Day of Harvest Boll Samples Collected: 12/23/83

Harvest Worker Exposure Monitoring Conducted: 12/23/83

Field # 10 Acres 140

Date	Pesticide
5/7	Kelthane-Sulfur 3-50
7/10	Supracide
7/18	Pydrin
7/26	Pydrin
8/2	Pydrin
8/10	Bolstar, Comite
8/19	Pydrin
8/26	Pydrin
9/2	Pydrin
9/9	Pydrin, Comite
9/16	Bolstar
9/24	Bolstar
10/1	Pydrin
11/3	DEF
11/22	Leafex

Predefoliation Boll Samples Collected: 10/27/83

Day of Harvest Boll Samples Collected: 01/04/84

Harvest Worker Exposure Monitoring Conducted: 01/04/84

APPENDIX I

Filters and Cotton Boll Analytical Methods

The sample is extracted three times by rotating for 30 minutes in a jar with 50 mL of ethyl acetate each. After evaporating the solvent, the pesticide is dissolved in 5 mL of hexane for GC analysis.

GC conditions:

Injector 250°F

DEF, Malathion, Dursban, Parathion, Curacron:
6 ft. 4% OV-101 at 180°, NP detector at 350°

Guthion, Bolstar:
6 ft. 4% OV-101 at 220°, NP detector at 350°

Pydrin, Ambush, Cymbush:
6 ft. 4% OV-101 at 220°, EC detector at 350°

Harvade:
6 ft. 2% OV-17 at 210°, FPD detector 300° S-mode

Calculation:

Cotton: Weight of sample: 10 g. Vol Injected - 0.6 uL; Peak Height - 101 (OHMAR - 9); STD - DEF 2 ng; Peak Height - 105

(2 ng) (101/105) (1/0.6 uL) (5000 uL/10 g) (ug/1000 ng) = 1.6 ppm

For filters the result is expressed in ug/sample.

APPENDIX II

Arsenic Determination by Atomic Absorption of Volatile Hydrides

SCOPE: This method can be used for any feed or fertilizer sample with an expected concentration of arsenic in the low ppm range.

PRINCIPLE: Arsine gas is generated by the use of sodium borohydride in an acid solution. The arsenic is determined by atomic absorption after being atomized in an air/acetylene flame.

EQUIPMENT AND REAGENTS: Varian 875 atomic absorption spectrometer
Varian Vapor Generator Model 65
Arsenic hollow cathode lamp
Standard Air/Acetylene burner
Strip chart recorder

Lamp current: 7 mA
Slit: 1.0 mm
Wavelength: 193.7 nm

Standard arsenic: 1,000 ppm As from Varian Associates. The stock solution is diluted with distilled water to give a working standard of 0.5 ppm As.

Sodium Borohydride: 98% pellets from Alfa Products.

ANALYSIS: Sample preparation: Organic samples: 1 to 10 grams are placed in a 400 mL beaker and digested on a hot plate with HNO_3 and 5 mL H_2SO_4 until clear. Inorganic samples: water soluble--dissolve 1 to 10 grams by heating on hot plate with distilled water. Others--digest in HCl or HNO_3 and H_2SO_4.

After dissolution, the sample is transferred to a 25 mL volumetric flask and made to volume with distilled water.

DETERMINATION: 1) An appropriate volume of sample (<15 mLs) is placed in the reaction vessel; 2) 10 mLs conc. HCl is added and the volume made up to 25 mLs with distilled water; 3) A sodium borohydride pellet is dropped into the reaction vessel; 4) The hydride is generated immediately and swept through the quartz tube. The arsenic peak is recorded on a strip chart recorder; 5) A standard curve is run in the same manner as the samples using 0.1 to 0.5 ug As; and, 6) A standard curve of ug As ug peak height is drawn and the As content of the sample is read off this curve.

CALCULATIONS:

$$\text{ppm As in samples} = \frac{\text{ug As from standard curve}}{\frac{\text{sample wt} \times \text{dilution} \times \text{aliquot (mLs)}}{25 \text{ mLs}}}$$

DISCUSSION: Note: If HNO_3 is used in the digestion, the sample must be boiled down to fumes of H_2SO_4 to expel the HNO_3. Nitric acid will prevent hydride generation.

REFERENCES: Ludmilla Duncan and Collin Parker, Applications of Sodium Borohydride for Atomic Absorption Determination of Volatile Hydrides, Technical Topics, Varian Techtron.

APPENDIX III

Arsenic in Urine [a/]

Digestion: 50 mL sample of urine
Add 25 mLs HNO_3.
" 1 mL H_2SO_4.
" 25 mLs 30% peroxide.
Reflux for 15 minutes.
Heat until evaporated to H_2SO_4.
Cool, add 4 mLs 30% peroxide.
Heat again - this should produce a clear solution.
Cool, add 5 mLs H_2O and heat to fumes of H_2SO_4 to drive off HNO_3 peroxide. (Repeat three times)
Cool, dilute to appropriate volume.
Continue with normal arsenic procedure.

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a/ Method from Margret Cunliff - Varian Applications Chemist, 9 January, 1984.

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